Another object of this invention is to provide an aqueous blackening solution which is simple to operate and which can be readily and safely handled in production operations by untrained personnel.

A distinct advantage of the invention is that black nickel coatings can be successfully applied to old, passive nickel deposits with or without preparatory cleaning, which permits processing of nickel plated objects that have been stored for extended periods of time, as frequently occurs in industry, as it is an inherent property of the blackening formulations disclosed herein that they have substantial capacity to re-activate nickel surfaces by removing passive nickel layers during the initial period of immersion in the solution, thus overcoming difficulties frequently encountered heretofore due to superficial nickel oxide films.

In accordance with the present invention, nickel objects, whether in sheet or other fabricated form, or having an electroplated deposit over a basis metal, may be given an adherent black coating by simply immersing them without the use of electric current in an aqueous solution containing an oxidizing agent belonging to the family of aromatic nitro derivatives and an inorganic salt of thiocyanic acid, together with a sufficient amount of a strong inorganic acid material to lower the pH of the solution to 2.0 or less. While some blackening will occur at room temperature in such solution, for all practical purposes the solution should be maintained at a minimum temperature of about 100° C. The process is operative at any temperature above this up to the boiling point of the solution.

In all cases the system will be suitable for blackening of nickel only so long as the pH is lowered to 2.0 or less, which may be accomplished by the addition of a suitable mineral acid. Various strong mineral acids are adequate, such as nitric or phosphoric, but sulfuric acid and its mono salts are preferred. The hydrogen ion concentration in solution should be at least 0.01 equivalent per liter, which will produce a pH of approximately 2.0, while higher concentrations are compatible with good functioning of the blackening solution up to around 1.0 equivalent per liter. Acid concentrations greater than 1.0 N give undesirable results and are outside the scope of the invention.

The aromatic nitro derivatives found useful for this invention include the water soluble sulfa, anilino, hydroxy and carbonyl substituted nitrobenzenes and nitronaphthalenes. Preferred compounds within this group include sodium m-nitrobenzenesulfonate and sodium m-nitrobenezote or the corresponding acids.

The thiocyanates found effective are the ammonium, sodium and potassium salts of the acid.

The following concentration ranges are successfully employed in applying black nickel coatings in accordance with this invention:

<table>
<thead>
<tr>
<th>Aromatic nitro derivative</th>
<th>Mole per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05 to 1.0</td>
</tr>
<tr>
<td>Inorganic thiocyanate</td>
<td>0.01 to 0.5</td>
</tr>
</tbody>
</table>

For purposes of further illustration of the invention, a preferred specific aqueous solution has the following composition:

| Sodium m-nitrobenzenesulfonate | 60 Grams per liter |
| Ammonium thiocyanate           | 5 Grams per liter  |
| Sulfuric acid (65% Baume)      | 2 Grams per liter  |

Such a solution, when used at temperatures above 100° F. to boiling, will produce attractive and adherent black coatings on metallic nickel objects by immersing the object in the solution for a short but sufficient period of time, usually of the order of 15 seconds to 5 minutes depend-
ing on the depth of color desired. Agitation of the solution or the objects will shorten the treatment time and is desirable but not essential.

A solution prepared in accordance with the foregoing specification, maintained at a temperature of 140° to 160° F., was employed in conducting each of the following tests:

**Example 1**

A brass plate plated with a 0.0002" deposit of bright nickel was immersed in the above solution. It was observed that the plate first turned a light brown which then deepened into an intense black after 1 minute of immersion time. Longer exposure to the solution resulted in further deepening of the black color which reached its highest intensity after 3 minutes, beyond which no noticeable change could be observed. The smoothness of the original nickel plate remained unaltered during the blackening operation which produced a black coating with high gloss.

**Example 2**

A steel panel plated with a 0.0003" deposit of bright nickel was immersed in successive steps in the above formulation at 150° F., while observing the effect at different immersion times ranging from 15 seconds to 3 minutes. It was found that after the initial 15 seconds, the coating turned an iridescent blue which, on longer exposure to the solution, changed to an intense black. The black was well adhered and after drying formed a suitable basis for painting, waxing, or other supplemental metal finishing operations.

**Example 3**

A specimen of zinc die casting was plated with a copper and then with a nickel deposit, and submitted to the above solution for about 2 minutes at approximately 150° F. The treatment resulted in a uniform, pleasing black color in the nickel deposit.

**Example 4**

A copper base metal item coated with bright nickel was immersed in the above formulation for 2 minutes, which gave the object a deep black color. After light buffing, the nickel took on a glossy, gray silvery appearance.

**Example 5**

A panel of Inconel alloy was adequately cleaned and immersed in the above formulation at 160° F. for 4 to 10 minutes. It was noted that blackening proceeded more slowly than with electrodeposited nickel coatings. However, after contacting the specimen with the solution for the above period of time, a satisfactory black coating developed on the surface of the panel.

In order to minimize the handling and shipping risks, it is frequently desired to provide a dry composition which can simply be added to water at such time as it is desired to treat the nickel or nickel plated objects to produce the black nickel coating thereon. Such a composition within the scope of this invention is readily provided as follows:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium m-nitrobenzoate</td>
</tr>
<tr>
<td>Ammonium thiocyanate</td>
</tr>
<tr>
<td>Sodium bisulfate</td>
</tr>
</tbody>
</table>

This composition, when added to water in amount sufficient to bring the resulting solution to a pH of 2.0 or less, operating at a solution temperature of around 140 to 160° F., produces very satisfactory results. Tests corresponding to those enumerated in Examples 1 through 5 above, substituting the last-mentioned formulation for that initially described in the foregoing examples, produces equivalent results in all cases.

Where the work to be blackened has just come out of the nickel plating bath, it should be carefully rinsed in cold water, whereupon it may then be immersed directly in the black nickel solution for the appropriate length of time. The dissolution of the nickel in solutions of the invention occurs at the rate of 0.0001" per minute at 160° F. Therefore, any work which has a nickel plate of minimum thickness of at least 0.0002"-0.0003" can be safely blackened. Following immersion in the blackening bath, the work is again rinsed in cold water and then allowed to air dry. The intensity of the black color is controlled by the length of the immersion time, increasing with longer periods of immersion. As already mentioned this black-coating may be subjected to further supplemental finishing, such as waxing, lacquering, oiling, color buffing, etc., to produce a pleasing satin appearance on the treated surface.

The solutions of the invention have exceptional capacity for accepting nickel goods whose surfaces have become oxidized through extended periods of storage. In such cases, the periods of immersion will generally be somewhat longer than those recommended hereinabove. If desired, the oxidized surfaces may be given a preliminary treatment, as by first subjecting them to soaking in any of a number of conventional alkaline cleaning solutions, then rinsing in water, followed by an acid dip and a further rinsing cycle.

Good rinsing of the parts after blackening is important in producing a uniform finish.

The invention has been described in connection with certain preferred embodiments but it is to be understood that these are illustrative rather than restrictive of the exact scope of the invention which is set out in the appended claims.

What is claimed is:

1. An aqueous solution for producing an adherent, black coating on nickel by reaction therewith, consisting essentially, in addition to water, of from 0.05 to 1.0 mole per liter of a water soluble compound selected from the group consisting of the sulfo, amino, hydroxy and carboxy substituted nitrobenzenes and nitronaphthalenes, from 0.01 to 0.5 mole per liter of a member selected from the group consisting of the ammonium and alkali metal salts of thiocyanate, together with a sufficient amount of a member selected from the group consisting of the mineral acids and the acid salts thereof to produce a hydrogen ion concentration in the solution of from 0.01 to 1.0 equivalent per liter.

2. An aqueous solution for producing an adherent, black coating on nickel as claimed in claim 1, wherein the substituted nitrobenzene compound is sodium m-nitrobenzene sulfonate, the thiocyanic acid salt is ammonium thiocyanate and the mineral acid is sulfuric.

3. An aqueous solution as defined in claim 2, wherein there is present in one liter of the solution approximately 60 grams of m-nitrobenzene sulfonate, 5 grams of ammonium thiocyanate and 2 grams of sulfuric acid (66° Baumé).

4. An aqueous solution for producing an adherent, black coating on nickel by reaction therewith consisting essentially, in addition to water, of approximately 60 grams of sodium m-nitrobenzoate, approximately 5 grams of ammonium thiocyanate and approximately 30 grams of sodium bisulfate, per liter of solution.

5. A dry composition for use in preparing an aqueous solution for producing an adherent, black coating on nickel by reaction therewith, said composition consisting essentially of twelve parts of sodium m-nitrobenzoate, one part of ammonium thiocyanate and six parts of sodium bisulfate, all of said parts being by weight.

6. The process of producing an adherent, black coating on nickel, which comprises immersing the nickel in an aqueous solution of the composition defined in claim 1, for a period of from 15 seconds to 10 minutes, while maintaining the temperature of the solution at from 100° F. to boiling.
7. The process of producing an adherent, black coating on nickel, which comprises immersing the nickel in an aqueous solution of the composition defined in claim 3, for a period of from 15 seconds to 10 minutes while maintaining the temperature of the solution at from 100°F to boiling.

8. The process of producing an adherent, black coating on nickel, which comprises immersing the nickel in an aqueous solution of the composition defined in claim 4, for a period of from 15 seconds to 10 minutes while maintaining the temperature of the solution at about 140°F to 160°F.